Legendre transforms for electrostatic energies

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Abstract

We review the use of Legendre transforms in the formulation of electrostatic energies in condensed matter. We show how to render standard functionals expressed in terms of the electrostatic potential, ϕ, convex – at the cost of expressing them in terms of the vector field $\mathbf{D}$. This leads to great simplification in the formulation of numerical minimisation of electrostatic energies coupled to other physical degrees of freedom. We also demonstrate the equivalence of recent functionals for dielectrics derived using field theory methods to classical formulations in terms of the electric polarisation.

I. INTRODUCTION

The Legendre transform is a powerful tool with multiple applications in physics [1]. In classical mechanics it allows one to interchange the Lagrangian and Hamiltonian viewpoints; in thermodynamics one regularly transforms ensembles to simplify calculations, choosing the ensemble which most closely idealizes a given experimental setup. In this article we will demonstrate the utility of Legendre transforms in reformulating energies and free energies in electrostatics, with a particular eye for numerical applications and mean field theory.

Our principal motivation for a deeper study of this transformation applied to electrostatic problems is quite practical. Many formulations of (free) energy functions in condensed matter physics involve the electrostatic potential, an important example is the Poisson-Boltzmann energy functional in the theory of ionic solutions. However when we examine closely these functionals we see that they are concave functions of the potential. While the stationary value of the functional is indeed the correct value of the energy that we wish to study, the concavity leads to complications in many situations. In particular we can not perform a simultaneous minimisation of both electrostatic and configurational energies in a simulation. One is generally obliged to fully solve by iterative methods the electrostatic problem at each time step of the iteration over the configurational degrees of freedom - such as densities or polymer configuration. This leads to codes which are complicated to write, and sometimes slow to run.

We remind the reader that for a convex function $f(x)$, its Legendre transform is defined [1] from the expression

$$\mathcal{L}\left[f\right](s) = g(s) = sx - f(x) \tag{1}$$

where on the right of eq. (1) we express x as a function of s from the equation $s = \frac{df}{dx}$. This transformation is an involution: $\mathcal{L}\left[g\right](x) = f(x)$. The simplest example is an Hookian spring for which $f(x) = kx^2/2$; then the transformation of eq. (1) gives $g(s) = s^2/(2k)$. We will also use the notation $\mathcal{L}(f) = \tilde{f}$. In this article we show that by introducing new variational parameters in a free energy with the help of Lagrange multipliers and then performing a Legendre transform of the resulting free energy we can find functionals that are convex in all degrees of freedom; we will illustrate this with a mean field formulation of phase separation coupled to electrostatic interactions.

We now illustrate the approach with the simplest possible electrostatic problem, interaction between free charges, ρ_f in a heterogeneous dielectric medium: Consider the energy functional expressed in terms of the electric potential ϕ.

$$U = \int \left\{ -\frac{\epsilon(\mathbf{r})(\nabla\phi)^2}{2} + \rho_f \phi \right\} d^3\mathbf{r} \tag{2}$$

The variational equation for the field is then the Poisson equation:

$$\text{div } \epsilon(\mathbf{r})\text{grad } \phi = -\rho_f(\mathbf{r}) \tag{3}$$

Substituting the solution of the Poisson equation in the electrostatic energy we find

$$U = \frac{1}{2} \int \phi(\mathbf{r})\rho_f(\mathbf{r}) \, d^3\mathbf{r} \tag{4}$$

We convert the variational problem for the potential by introducing the new variable $\mathbf{E} = -\nabla\phi$. To do so we introduce the (vector) Lagrange multiplier $\mathbf{D}$. The stationary point of eq. (2) is identical to that of the following expression [2]:

$$U = \int \left\{ -\frac{\epsilon(\mathbf{r})\mathbf{E}^2}{2} + \rho_f\phi + \mathbf{D} \cdot (\mathbf{E} + \nabla\phi) \right\} \, d^3\mathbf{r} \tag{5}$$

It is at this point that we recognise that the variational equations for $\mathbf{E}$ correspond to a Legendre transform with dual variable $\mathbf{D}$. We also integrate by parts the product $\mathbf{D} \cdot \nabla\phi$ to find $-\phi \, \text{div } \mathbf{D}$, dropping boundary terms assumed to be zero. Thus the stationary point of eq. (2) is identical to the stationary point of

$$U = \int \left\{ \frac{\mathbf{D}^2}{2\epsilon(\mathbf{r})} + \phi(\rho - \text{div } \mathbf{D}) \right\} \, d^3\mathbf{r} \tag{6}$$

Variations in ϕ now impose Gauss' law, $\text{div } \mathbf{D} - \rho_f = 0$, while the energy has been rendered convex by the transformations introduced, [3, 4].

We now illustrate applications of this transformation to two problems: Firstly the theory of phase separation of immiscible fluids in the presence of electrostatic interactions due to ions. Secondly we provide a translation between two very different visions of the theory of dielectrics. Recent formulations of implicit dielectrics pass by elaborate field-theory mappings and find a generalised Poisson-Boltzmann equation with a Langevin correction. We show how to map this description onto a free energy expressed in terms of a polarisation field with long-ranged dipolar interactions. We believe that these equivalent descriptions can lead to a deeper understanding of the underlying physics.

In the following we will work with free energy densities, rather than the integrated energies and we (silently) integrate by parts when needed.

II. PHASE SEPARATION COUPLED TO ELECTROSTATICS

A mixture of two solvents (A and B) near their miscibility limit and in the presence of salt displays interesting properties which have been explored in recent experiments [5]. Density fluctuations couple to the dielectric properties of the medium, and in turn influence the partition of ions in the fluctuating solvent field. The experimental system has turned out to be very rich, and allows one to adjust the effective interaction between colloidal particles using temperature as a control parameter.

A simplified theoretical description of such systems is given in [6, 7] who propose the following free energy density expressed in terms of the densities and potentials:

$$f(\phi, \Psi, c_+, c_-) = f_m(\Psi) - \frac{1}{2}\epsilon(\Psi)(\nabla\phi)^2 + (c_+ - c_-)e\phi$$
$$- \left(\Delta u^+ c_+ + \Delta u^- c_-\right)\Psi + k_B T \sum_j (c_j \ln (c_j/c_{j0}) - c_j) \tag{7}$$

Ψ describes the composition fluctuations of the fluid mixture. c_+ and c_- are the concentration of positive and negative monovalent ions, with Δu^+ and Δu^- their relative preferences between

a A-liquid environment and a B-liquid environment. As above ϕ is the electrostatic potential. We see that fluctuations in concentration couple via $\epsilon(\Psi)$ to a coupling with the concentration fluctuations of the ions.

$f_m(\Psi)$ includes all the terms that are only dependent on Ψ: $f_m(\Psi) = f_0(\Psi) + \frac{c}{2}(\nabla\Psi)^2 - \mu\Psi$; with $f_0(\Psi)$ the free energy due to the mixing of the two solvents. It can, for exemple, be written as a binary mixture free energy density: $f_0(\Psi) \propto \Psi\log(\Psi) + (1-\Psi)\log(1-\Psi) + \chi\Psi(1-\Psi)$, with χ the Flory parameter [8, 9], or as a Landau expansion $f_0(\Psi) \propto \alpha(\Psi - \Psi_c)^2 + \gamma(\Psi - \Psi_c)^4$, with α being temperature dependent, γ positive, and Φ_c the critical composition [6].

Optimising eq. (7) over c_+ and c_-, the density becomes :

$$f(\Psi, \phi) = f_m(\Psi) - \frac{1}{2}\epsilon(\Psi)(\nabla\phi)^2 - k_B T c_{0+}\exp(\beta\Delta u^+ \Psi - \beta e\phi)$$
$$- k_B T c_{0-}\exp(\beta\Delta u^- \Psi + \beta e\phi) \tag{8}$$

With a symmetric electrolyte: $c_{0+} = c_{0-}$, and if we assume the ions are similar in their interaction with the solvents : $\Delta u^+ = \Delta u^-$, $f(\Psi, \phi)$ simplifies into :

$$f(\Psi, \phi) = f_m(\Psi) - \frac{1}{2}\epsilon(\Psi)(\nabla\phi)^2 - 2k_B T c_0 \exp(\beta\Delta u\Psi)\cosh(\beta e\phi) \tag{9}$$

We recognise here a generalisation of the well known Poisson-Boltzmann functional for a symmetric electrolyte. The description is adapted to analytical solutions but in the monophase region of the phase diagram $f(\Psi, \phi)$ is convex in Ψ but concave in ϕ. In complicated geometries if one wishes to minimize this free energy numerically one has to solve saddle point equations, simple minimization will not give the correct answer. We now implement the transformation introduced above from the potential ϕ to the electric displacement $\mathbf{D}$ and use the fact that the Legendre transform of cosh is :

$$\mathcal{L}[A\cosh(B\phi)](\xi) = A\left[\xi/(AB)\text{asinh}\,(\xi/AB) - \sqrt{(\xi/AB)^2 + 1}\right]$$
$$= Ag\,(\xi/AB) \tag{10}$$

After some calculation we find

$$f(\Psi, \mathbf{D}) = f_m(\Psi) + \frac{\mathbf{D}^2}{2\epsilon(\Psi)} + 2k_B T c_0 e^{\beta\Delta u\Psi} g\left(\frac{\text{div}\,(\mathbf{D})e^{-\beta\Delta u\Psi}}{2c_0 e}\right) \tag{11}$$

We have thus reached our objective: we have built an equivalent description of the system with the stationary conditions conserved and a local and convex function. The disadvantage is that there are more degrees of freedom in the vector field $\mathbf{D}$ than in the scalar field ϕ, but the advantage is that a global minimising principle can be used and the functional can be directly programmed for the solution of the coupled electrostatic-phase separation problem.

We note that mean field description of the packing of DNA in a virus [10] contains many similar theoretical features and is also amenable to similar transformations. In this problem the field Ψ corresponds to the square root of the monomer density.

III. FROM POISSON-LANGEVIN TO POLARIZATION

We now consider theories of explicit Langevin dipoles and how these can be incorporated into the formulation of the free energy in terms of convex free energy functions. Recent work on improving the description of solvation of proteins [11] has considered an explicit model for the solvent in terms of Langevin dipoles. If we neglect the volume of ions and dipoles they find the free energy density for a mixture of symmetric ions and neutral dipoles :

$$f = \rho_f \phi - \frac{\epsilon_0(\nabla\phi)^2}{2} - 2\lambda_{ion}\cosh(\beta q\phi) - \lambda_{dip}\frac{\sinh(\beta p_0|\nabla\phi|)}{\beta p_0|\nabla\phi|} \tag{12}$$

3

where to simplify the presentation we have neglected effects of finite ion size. The parameters λ are related to the chemical activities of the ions and the dipoles.

As in previous work [12] we start by using a Lagrangian multiplier, $\mathbf{D}$ to replace $(\nabla\phi)$ by its electrostatic equivalent $-\mathbf{E}$. We find

$$f = \rho_f \phi - \frac{\epsilon_0 \mathbf{E}^2}{2} - g(\phi) - h(\mathbf{E}) + \mathbf{D} \cdot (\nabla\phi + \mathbf{E}) \tag{13}$$

where $h(\mathbf{E})$ is the free energy density due to the dipoles and $g(\phi)$ the free energy due to free ions. We now diverge from our previous treatment and introduce a new variable $\mathbf{P}$ which we will show is the physical polarisation variable. We do this by performing a Legendre transform on $h(\mathbf{E})$ to find $\tilde{h}(\mathbf{P})$; we then find

$$f = \phi(\rho_f - \operatorname{div} \mathbf{D}) - \frac{\epsilon_0 \mathbf{E}^2}{2} - g(\phi) + \tilde{h}(\mathbf{P}) + \mathbf{E} \cdot (\mathbf{D} - \mathbf{P}) \tag{14}$$

Clearly by definition of the Legendre transform performing variations with respect to $\mathbf{P}$ on eq. (14) gives eq. (13).

We now perform two more transforms firstly to eliminate the potential, but secondly to eliminate the electric field $\mathbf{E}$. We find

$$f = \frac{(\mathbf{D} - \mathbf{P})^2}{2\epsilon_0} + \tilde{h}(\mathbf{P}) + \tilde{g}(\rho_f - \operatorname{div} \mathbf{D}) \tag{15}$$

In the absence of free ions the function $\tilde{g}$ reduces to the constraint of Gauss' law. This is exactly the form postulated in [13]. It is particularly transparent for understanding the physical limits on response functions [14, 15] and the origin of the negative dielectric constant observed in structured fluids.

We will now work from eq. (15) to demonstrate its equivalence to other formulations of electrostatic interactions expressed in terms of the polarization $\mathbf{P}$. To do this we will eliminate the variable $\mathbf{D}$, which will bring us back to other more familiar forms for the electrostatic energy at the cost of re-introducing long-ranged dipole-dipole interactions between the polarization variables.

Eliminating the Displacement field

Let us work in the limit where linear response is valid, in which case we expand $\tilde{h}$ to quadratic order:
$$\tilde{h}(\mathbf{P}) = \frac{\mathbf{P}^2}{2\epsilon_0 \chi} \tag{16}$$

where χ is a material parameter. Taking variations of eq. (14) with respect to $\mathbf{P}$ and then $\mathbf{E}$ we find that

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E}, \quad \epsilon_0 \mathbf{E} = \mathbf{D} - \mathbf{P} \tag{17}$$

Thus the parameter χ is the electric susceptibility of the medium. The polarisation variable is indeed playing the role we expect from standard treatments of Maxwell's equations. The free energy of the fluctuating dipoles (in the absence of free ions) can then be found from the functional

$$f = \frac{(\mathbf{D} - \mathbf{P})^2}{2\epsilon_0} + \frac{\mathbf{P}^2}{2\epsilon_0 \chi(\mathbf{r})} - \phi(\operatorname{div} \mathbf{D} - \rho_f) \tag{18}$$

where the last term is a Lagrange multiplier for the constraint of Gauss' law. On taking variations of eq. (18) with respect to $\mathbf{D}$ we find that

$$\mathbf{D} - \mathbf{P} = -\epsilon_0 \nabla\phi \tag{19}$$

4

Thus the free energy density can be written as

$$f = \epsilon_0 \frac{(\nabla\phi)^2}{2} + \frac{\mathbf{P}^2}{2\epsilon_0\chi} \tag{20}$$

where

$$\epsilon_0 \nabla^2 \phi = -\rho_f + \text{div } \mathbf{P}$$
$$\phi(\mathbf{r}) = \int \frac{1}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} \left(\rho(\mathbf{r}') - \text{div } \mathbf{P}(\mathbf{r}')\right) \, d^3\mathbf{r}' \tag{21}$$

We now substitute eq. (21) in eq. (20) and introduce the bare electric field $\mathbf{E}_0$ as follows: $\mathbf{E}_0 = -\nabla\phi_0$ with $\epsilon_0 \nabla^2 \phi_0 = -\rho_f$. The free energy density can then be expressed in terms of the polarization as

$$U = \frac{1}{2} \int \frac{\text{div } \mathbf{P}(\mathbf{r}) \text{div } \mathbf{P}(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} \, d^3\mathbf{r} \, d^3\mathbf{r}' +$$
$$\int \left\{ \frac{\epsilon_0 \mathbf{E}_0^2}{2} - \mathbf{E}_0 \cdot \mathbf{P} + \frac{\mathbf{P}^2}{2\epsilon_0\chi(\mathbf{r})} \right\} \, d^3\mathbf{r} \tag{22}$$

This formulation of the free energy is widely used in theoretical chemistry and is that used by [16]

The energy eq. (22) can be expressed in an even more physically transparent manner by integrating by parts the first double integral to transfer the derivatives from the polarization to the function $1/|\mathbf{r}-\mathbf{r}'|$. If we do this we find that the double integral is transformed to

$$\frac{1}{2} \int \mathbf{P}(\mathbf{r}) T(\mathbf{r}-\mathbf{r}') \mathbf{P}(\mathbf{r}') \, d^3\mathbf{r} \, d^3\mathbf{r}' \tag{23}$$

where the dipole operator is

$$T(\mathbf{r}) = \left[\frac{1 - 3|\mathbf{r}\rangle\langle\mathbf{r}|}{4\pi r^3 \epsilon_0} + \frac{\delta(\mathbf{r})}{3\epsilon_0} \right] \tag{24}$$

We now proceed in a more abstract manner, considering that the polarisation variables are assembled into a vector and the dipolar interactions form a matrix, $\bar{T}$. Eq. (22) is simply a quadratic form in $\mathbf{P}$, so that

$$U = \frac{\mathbf{P}(\bar{K}+\bar{T})\mathbf{P}}{2} - \mathbf{E}_0 \cdot \mathbf{P} + \epsilon_0 \frac{\mathbf{E}_0^2}{2} \tag{25}$$

with the diagonal matrix $\epsilon_0 K_{\mathbf{r},\mathbf{r}} = \chi_{\mathbf{r}}^{-1}$. If we now calculate the response of the polarization field to an external perturbation $\mathbf{E}_0$ we find

$$\mathbf{P} = \frac{1}{\bar{K}+\bar{T}} \mathbf{E}_0 \tag{26}$$

The total electric field is then given by two contributions, the original imposed field $\mathbf{E}_0$ and that due to the dipole density $\mathbf{P}$:

$$\mathbf{E} = \mathbf{E}_0 - \bar{T}\mathbf{P} \tag{27}$$

$$= \frac{\bar{K}}{\bar{K}+\bar{T}} \mathbf{E}_0 \tag{28}$$

We also use

$$\mathbf{D} - \mathbf{P} = \epsilon_0 \mathbf{E} \tag{29}$$

5

to find

$$\mathbf{D} = \frac{I + \epsilon_0 \bar{K}}{\bar{K} + \bar{T}} \mathbf{E}_0 \tag{30}$$

Again all these equations are non-local - since they involve the long-ranged operator $\bar{T}$ but we find that

$$\mathbf{D} = (1 + \chi_{\mathbf{r}})\epsilon_0 \mathbf{E} = \epsilon \mathbf{E} \tag{31}$$

a purely local constitutive equation between the electric field and the electric displacement.

We conclude that by careful study of the mean field equations coming from the formulation of the dielectric properties of a medium in eq. (12) we have been able to derive the equivalence to the standard continuum formulation of electrostatic arising from Maxwell's equations.

IV.   Conclusions

We have shown that the Legendre transform can be used to translate between multiple forms of the energy in mean-field theories. All the formulations are numerically equivalent but different forms put the emphasis on different degrees of freedom in electromagnetism. For numerical work it is advantageous to work with a formulation which is both convex and local. This is achieved in Poisson-Boltzmann theory by choosing the electric displacement $\mathbf{D}$ as the fundamental thermo-dynamic field. In this way all physical degrees of freedom can be treated in an equivalent manner in numerical solvers. It is no longer necessary to completely solve the electrostatic problem for each iteration of other external degrees of freedom. Very similar conclusions have also been found in quantum chemistry [17]

We have also demonstrated that energy functionals for dielectrics can be translated into equivalent forms by introducing the physical polarization. We then mapped a linearised form of the theory to the Marcus energy function, widely used in the theoretical chemistry literature.

IV.References

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